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PHOTOCHEMISTRY OF σ-ALLYL COMPLEXES OF MANGANESE AND TUNGSTEN IN FROZEN GAS MATRICES AT ca. 12 K. INFRARED SPECTROSCOPIC EVIDENCE FOR PHOTODECARBONYLATION AND σ → π CONVERSION PROCESSES

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Summary

Infrared spectroscopy, together with ^{13}CO enrichment and energy-factored force-field fitting of terminal CO stretching bands, has been employed to study the photochemistry of $Mn(\eta^1\text{-}C_3H_5)(CO)_5$ and $W(\eta^1\text{-}C_3H_5)(\eta^5\text{-}C_5H_5)(CO)_3$ isolated at high dilution (1/2000 to 1/5000) in various gas matrices at ca. 12 K. For the Mn complex ejection of a CO ligand was concomitant with σ → π rearrangement to afford $Mn(\eta^3\text{-}C_3H_5)(CO)_4$ which lost a further CO reversibly to give $Mn(\eta^3\text{-}C_3H_5)(CO)_3$. In N_2 matrices the unsaturated species picked up an N_2 ligand to yield $Mn(\eta^3\text{-}C_3H_5)(CO)_3(N_2)$ while in CO matrices its reaction with CO was so facile that no $Mn(\eta^3\text{-}C_3H_5)(CO)_3$ could be detected. In contrast, the W complex confirmed that CO ejection and σ → π rearrangement occurred in two steps by virtue of the isolation of the 16-electron species $W(\eta^1\text{-}C_3H_5)(\eta^5\text{-}C_5H_5)(CO)_2$. For W, however, the η^3-allyl complex did not seem to undergo further CO loss to give $W(\eta^3\text{-}C_3H_5)(\eta^5\text{-}C_5H_5)(CO)$. The two step process seen for W, together with the facile reversal $W(\eta^1\text{-}C_3H_5)(\eta^5\text{-}C_5H_5)(CO)_2 \rightleftarrows W(\eta^3\text{-}C_3H_5)(\eta^5\text{-}C_5H_5)(CO)_2$, indicates that η^1- → η^3-allyl rearrangements in general proceed in solution by two step reactions even when the intermediate stages cannot be observed. Such a two step process will have implications for kinetic studies. Attempts to enrich $Mn(\eta^1\text{-}C_3H_3)(CO)_5$ with ^{13}CO in solution and in ^{13}CO doped CH_4 matrices resulted in no ^{13}CO incorporation. It is suggested that Mn has a preference for an η^3-allyl ligand and that σ → π rearrangement is irreversible in this case.

Three types of allyl complexes of transition metals have been identified: σ-allyl (σ-C_3H_5 or η^1-C_3H_5), π-allyl (π-C_3H_5 or η^3-C_3H_5), and allyl bridged (μ-C_3H_5) complexes [1]. In the η^1-allyl complexes the allyl ligand contributes 1-electron to the metal–allyl bond to give a conventional carbon–metal two-electron linkage, whereas in the η^3-allyl compounds the allyl ligand may be regarded as contributing 3-elec-

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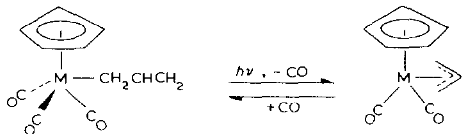
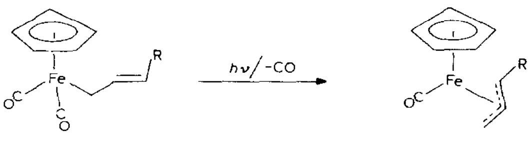
trons to the metal–allyl bond. Consequently, this results in a stronger bond between a metal and an allyl ligand for η^3-allyl complexes than for the η^1-allyl complexes. In general, the η^1-allyl complexes are thermally less stable and may decompose to form η^3-allyl complexes. For example, although $Mn(\eta^1\text{-}C_3H_5)(CO)_5$ and $Mn(\eta^3\text{-}C_3H_5)(CO)_4$ are known stable complexes [2,3] for Co only $Co(\eta^3\text{-}C_3H_5)(CO)_3$ has been isolated [3,4]. The $Co(\eta^1\text{-}C_3H_5)(CO)_4$ complex presumably decarbonylates even at room temperature to give the η^3-allyl complex. Interestingly the Co perfluoroallyl complex $Co(\eta^3\text{-}C_3F_5)(CO)_4$ when reacted with PPh_3 gave a trigonal bipyramidal η^1-complex, $Co(\eta^1\text{-}C_3F_5)(CO)_3(PPh_3)$, as a minor product [4,5].

A $\sigma \rightarrow \pi$ rearrangement is an intramolecular reaction in which an organic group σ-bonded (η^1) to a metal becomes π-bonded (η^n) and this process is often reversible. Such $\sigma \rightleftarrows \pi$ rearrangements are also very important in organic syntheses [6] and homogeneous catalytic process [7,8]. For example, when the σ-allyl complexes $M(\eta^1\text{-}C_3H_5)(\eta^5\text{-}C_5H_5)(CO)_3$ (M = Mo [9], W [10]) are irradiated with UV light a $\sigma \rightarrow \pi$ rearrangement occurs, yielding the π-allyl complexes. Upon addition of CO a $\pi \rightarrow \sigma$ rearrangement is observed (eq. 1).



(1)

Interesting consequences of CO dissociation from substituted allyl complexes e.g. $Fe(\eta^5\text{-}C_5H_5)(CO)_2(\eta^1\text{-}C_3H_4R)$, include *syn* and *anti* conformations of the R group



(2)

after $\sigma \rightarrow \pi$ rearrangement (eq. 2) [9]. In most cases the thermal and photochemical $\sigma \rightarrow \pi$ rearrangements are irreversible, e.g. eq. 3 [1–3], but in principle, the process

$$Mn(\eta^1\text{-}C_3H_5)(CO)_5 \xrightarrow{\Delta \text{ or } h\nu} Mn(\eta^3\text{-}C_3H_5)(CO)_4 + CO \qquad (3)$$

should be reversible as for Mo and W allyl complexes (eq. 1). An example of a reversible process was found with $Co(\eta^3\text{-}C_3H_5)(CO)_4$ isolated in a CO matrix at ca. 12 K (eq. 4) [11]. The detection of $Co(\eta^1\text{-}C_3H_5)(CO)_4$ was taken as evidence that there could be an S_N2 contribution to the ligand substitution reactions whereas previously only an S_N1 path had been considered.

$$Co(\eta^3\text{-}C_3H_5)(CO)_3 \underset{-CO}{\overset{h\nu,\ +CO}{\rightleftarrows}} Co(\eta^1\text{-}C_3H_5)(CO)_4 \qquad (4)$$

The matrix isolation technique [12] has proved to be very apt at characterising unstable species, particularly unstable organometallic species some of which have been proposed as intermediates and transition state species in thermal and photochemical reactions [13,14]. In this paper we report the photochemistry of $Mn(\eta^1\text{-}C_3H_5)(CO)_5$ and $W(\eta^1\text{-}C_3H_5)(\eta^5\text{-}C_5H_5)(CO)_3$ isolated at high dilutions in various frozen gas matrices at ca. 12 K. The results are discussed in relation to room temperature solution reactions and are also compared with the chemistry of related compounds e.g. $Co(\eta^3\text{-}C_3H_5)(CO)_3$ and $W(\eta^1\text{-}CH_2Ph)(\eta^5\text{-}C_5H_5)(CO)_3$.

Experimental

The cryogenic equipment and vacuum systems, matrix gases, infrared and UV-VIS spectrometers and the medium pressure mercury arc photolysis lamp have been described elsewhere [15]. Wavelength-selective photolyses in this study were achieved by using the following combinations of adsorbing materials: filter A, $320 < \lambda < 390$ nm, Corning glass colour filter CS 7-60 (3 mm thick); filter B, $230 < \lambda < 280$ nm, Corning glass colour filter CS 7-54 (3 mm thick) + quartz gas cell (pathlength 25 mm) containing Cl_2 (2 atm); filter C, $\lambda > 420$ nm, Corning glass colour filter CS 3-74 (3 mm thick); filter D, $290 < \lambda < 370$ and $\lambda > 550$ nm, quartz gas cell (pathlength 25 mm) containing Br_2 (300 Torr) + pyrex disc (3 mm thick); filter E, $\lambda > 370$ nm, Corning glass filter CS 0-51 (3 mm thick).

The sample of $Mn(\eta^1\text{-}C_3H_5)(CO)_5$ was a gift from Dr. G.F. Griffin and was used without further purification. It was found to have $Mn(\eta^3\text{-}C_3H_5)(CO)_4$ present as an impurity or as a decomposition product. Matrices were prepared by making gas mixtures (in 1 l bulb) comprising the vapour of the complex (vapour pressure at ca. 0°C) and matrix gas (150 Torr) using a vacuum line and standard manometric techniques. The resulting mixtures had a composition with ratios of substrate/host matrix gas in the range 1/2000–1/5000. The gas mixtures were deposited onto cooled CsI or CaF_2 windows by the pulsing method.

The sample of $W(\eta^1\text{-}C_3H_5)(\eta^5\text{-}C_5H_5)(CO)_3$ was a gift from Dr. H.G. Alt and was used without further purification. The complex was not volatile enough to make up gas mixtures, cf. $Mn(\eta^1\text{-}C_3H_5)(CO)_5$, and so matrices were prepared by co-condensing the vapour of the complex held in a glass spray-on head (ca. 30°C) [16] together with a vast excess of matrix gas. High dilution was indicated by narrow bands ($\sim 3\ cm^{-1}$ wide at half-absorbance) with no tailing to lower wavenumbers.

Results

Photolysis of $Mn(\eta^1\text{-}C_3H_5)(CO)_5$ in CH_4 and Ar matrices

The electronic absorption spectrum of $Mn(\eta^1\text{-}C_3H_5)(CO)_5$ isolated at high dilution in a CH_4 matrix at ca. 12 K shows strong and medium absorption bands at 215 and 270 nm respectively (Fig. 1(a)). By analogy with $Mn(CO)_5CH_3$ these absorption bands may be assigned as metal → ligand charge-transfer bands [17] i.e. from e_π molecular orbitals of the metal to $\pi^*(CO)$ levels which do not interact with manganese orbitals.

The infrared spectrum of $Mn(\eta^1\text{-}C_3H_5)(CO)_5$ isolated at high dilution in a CH_4 matrix at ca. 12 K is shown in Fig. 2(a). The spectrum is very similar to that observed in cyclohexane solution [18] and indicates that the $Mn(CO)_5$ fragment has approximate C_{4v} local symmetry ($\nu(CO) = 2A_1 + B_1 + E$; Table 1). The most in-

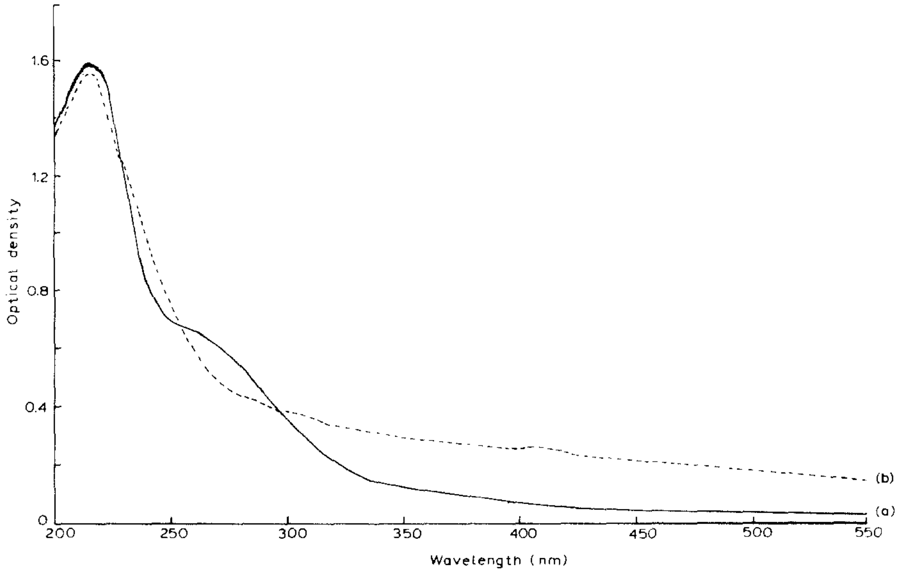


Fig. 1. Electronic absorption spectra (Pye Unicam SP 1800B) for Mn(η^1-C_3H_5)(CO)$_5$ isolated at high dilution in a CH_4 matrix at ca. 12 K: (a) After deposition, and (b) after 30 min UV irradiation (filter B).

tense band at 2012.4 cm^{-1} corresponds to the E mode. The two A_1 vibrations consist of the vibration of the axial CO ligand and the symmetric breathing mode of the equatorial CO ligands. Thus, the highest wavenumber band at 2108.9 cm^{-1} correspond to the $A_1(eq)$ mode and the lower band at 1988.5 cm^{-1} corresponds to the $A_1(ax)$ mode. The weak band at 2048.0 cm^{-1} may be assigned to the B_1 band which is forbidden in the infrared spectrum under strict C_{4v} symmetry. Its appearance, however, indicates a slight perturbation resulting from the asymmetry of the σ-allyl group, cf. the asymmetry caused by the σ-acetyl group in Mn(CO)$_5$(COCH$_3$) [19]. The positions of the IR bands of Mn(η^1-C_3H_5)(CO)$_5$ are almost identical to those of Mn(CO)$_5$CH$_3$ in a CH_4 matrix [19] except that the B_1 band is not seen in the more symmetrical methyl compound. Therefore, the bonding of the CO ligands in Mn(η^1-C_3H_5)(CO)$_5$ and Mn(CO)$_5$CH$_3$ would seem to be approximately the same. Bands marked Q (Figs. 2, 3, 5 and 6) are due to Mn(η^3-C_3H_5)(CO)$_4$, present as an impurity or as a decomposition product, which has C_s symmetry (ν(CO) = $3A' + A''$) [20,21].

Brief near UV irradiation (filter A) resulted in decreases in the intensities of bands due to Mn(η^1-C_3H_5)(CO)$_5$, increases in the intensities of bands due to Mn(η^3-C_3H_5(CO)$_4$, and production of 'free' CO at 2138.0 cm^{-1} (Fig. 2(b)). Further far UV irradiation (filter B) caused enormous intensity reductions in the bands of Mn(η^1-C_3H_5)(CO)$_5$ and Mn(η^3-C_3H_5)(CO)$_4$ with the production of more 'free' CO and the appearance of three new bands at 2031.5, 1950.2 and 1924.3 cm^{-1} (Fig. 2(c)). The electronic spectrum at this stage (Fig. 1(b)) shows the disappearance of the parent absorption at 270 nm with concomitant appearance of a strong absorption at 235 nm and possibly two weak absorptions at 310 and 410 nm. Irradiation with visible light (filter C) or annealing the matrix to ca. 35 K (Figs. 2(d) and 2(e) respectively) resulted in reductions in intensities of 'free' CO and the three new

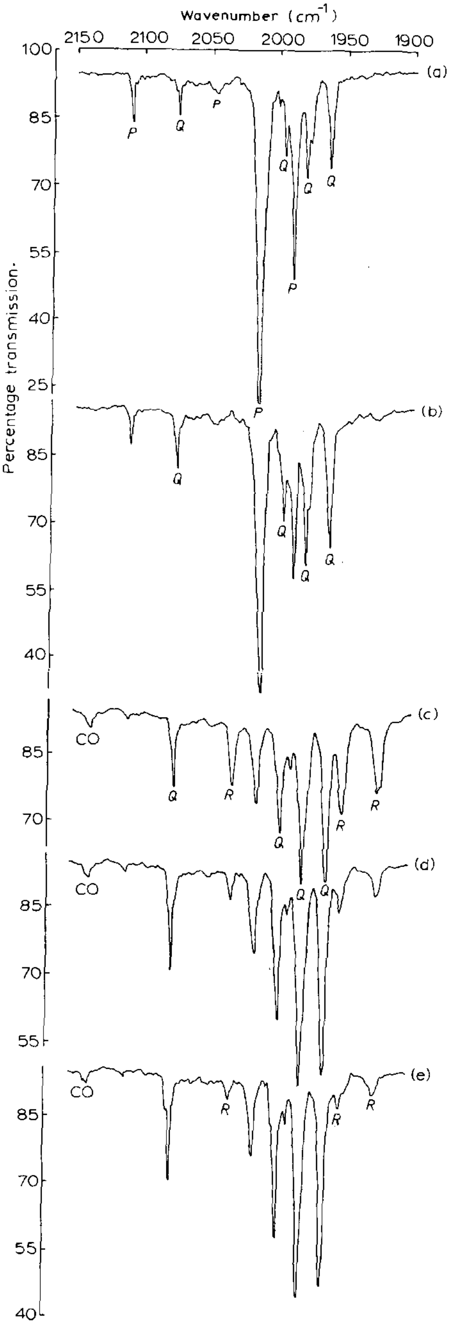


Fig. 2. Infrared spectra (Nicolet FTIR 7199) from an experiment with Mn(η^1-C_3H_5)(CO)$_5$ isolated at high dilution in a CH_4 matrix at ca. 12 K: (a) after deposition, (b) after 15 min UV irradiation (filter A), (c) after further 15 min UV irradiation (filter B), (d) after 2 h visible irradiation (filter C), and (e) after annealing to ca. 35 K. Labelled bands are: P = Mn(η^1-C_3H_5)(CO)$_5$, Q = Mn(η^3-C_3H_5)(CO)$_4$, R = Mn(η^3-C_3H_5)(CO)$_3$.

TABLE 1

OBSERVED INFRARED-ACTIVE TERMINAL CO STRETCHING BAND POSITIONS (cm^{-1}) FOR $Mn(\eta^1-C_3H_5)(CO)_5$ AND $W(\eta^1-C_3H_5)(\eta^5-C_5H_5)(CO)_3$ AND THEIR PHOTOPRODUCTS IN VARIOUS GAS MATRICES AT ca. 12 K

Compound	ν(CO)	CH_4	Ar	N_2	CO
$Mn(\eta^1-C_3H_5)(CO)_5$	A_1	2108.9	2112.3	2111.9	2109.4
	B_1 [a]	2048.0	2052.5	2051.9	2048.6
C_{4v}	E	2012.4	2018.6 2016.8 [b]	2015.8	2012.9
	A_1	1988.5	1992.8	1991.0	1990.1
$Mn(\eta^3-C_3H_5)(CO)_4$	A'	2074.7	2083.1	2083.1	2081.3
	A'	1995.8	2004.4 2002.5 [b]	2002.5	2001.3
C_s	A''	1979.2	1986.3	1985.6	1983.8
	A'	1961.5	1971.9	1967.5	1965.8
$Mn(\eta^3-C_5H_5)(CO)_3$	A'	2031.5	2040.6		
C_s	A'	1950.2	1960.0		
	A''	1924.3	1932.5		
$Mn(\eta^3-C_3H_5)(CO)_3(N_2)$ [c,d]				2018.8	
				1960.0	
$W(\eta^1-C_3H_5)(\eta^5-C_5H_5)(CO)_3$	A'	2019.3			
C_s	A'	1934.0			
	A''	1924.0			
$W(\eta^1-C_3H_5)(\eta^5-C_5H_5)(CO)_2$	A'	1951.8			
C_s	A''	1866.5			
$W(\eta^3-C_3H_5)(\eta^5-C_5H_5)(CO)_2$	A	1960.2			
C_1	A	1882.5			

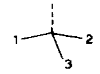
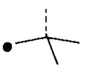
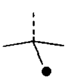
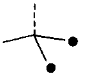
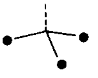
[a] Infrared inactive; appearance is indicative of slight perturbation. [b] Matrix splitting. [c] ν(NN) at 2256.9 cm^{-1}. [d] Structure not fully established.

bands, increases in the intensities of bands of $Mn(\eta^3-C_3H_5)(CO)_4$, while the intensities of the bands of $Mn(\eta^1-C_3H_5)(CO)_5$ remained unchanged. The dilution used (1/2000–1/5000) and the reversibility of the matrix reaction rule out the possibility of any aggregate formation. Since the relative intensities of the new bands at 2031.5, 1950.2 and 1924.3 cm^{-1} remained constant under a variety of photolysis cycles, i.e. growing and decreasing at the same rate, these bands belong to a single mononuclear species. The fact that 'free' CO has been generated suggests that the new species is derived from further decarbonylation of $Mn(\eta^3-C_3H_5)(CO)_4$, i.e. the new photoproduct is probably $Mn(\eta^3-C_3H_5)(CO)_3$ (Table 1). The identity of the $Mn(\eta^3-C_3H_5)(CO)_3$ was confirmed by a ^{13}CO labelling experiment (see below). The reactivity of the coordinatively unsaturated 16-electron species $Mn(\eta^3-C_3H_5)(CO)_3$ is demonstrated by its photochemical and thermal recombination with CO to form $Mn(\eta^3-C_3H_5)(CO)_4$ upon visible photolysis and annealing respectively.

Analogous observations have been recorded for Ar matrices (Table 1) but with a slower photoreaction rate. UV irradiation caused expulsion of CO from $Mn(\eta^1-C_3H_5)(CO)_5$ to form $Mn(\eta^3-C_3H_5)(CO)_4$, and further loss of CO subsequently produced the 16-electron species $Mn(\eta^3-C_3H_5)(CO)_3$.

TABLE 2

OBSERVED AND CALCULATED [a] INFRARED BAND POSITIONS (cm^{-1}) OF TERMINAL CO STRETCHING BANDS FOR $Mn(\eta^3\text{-}C_3H_5)(^{12}CO)_{3-n}(^{13}CO)_n$ ($n = 0\text{–}3$) GENERATED FROM ^{13}CO ENRICHMENT EXPERIMENTS WITH $Mn(\eta^1\text{-}C_3H_5)(CO)_5$ ISOLATED AT HIGH DILUTION IN ^{13}CO DOPED (5%) CH_4 MATRICES AT ca. 12 K

Compound	^{13}CO position (●)	$\nu(CO)$	Observed	Calculated
$Mn(\eta^3\text{-}C_3H_5)(^{12}CO)_3$		A'	2031.2	2030.4
C_s		A'	1950.2	1951.2
	1 ≠ 2 = 3	A''	1924.1	1924.7
$Mn(\eta^3\text{-}C_3H_5)(^{12}CO)_2(^{13}CO)$		A'	2008.9	2007.7
C_s		A'	1931.9	1929.4
		A''	1923.8	1924.7
$Mn(\eta^3\text{-}C_3H_5)(^{12}CO)_2(^{13}CO)$		A	2023.5	2024.6
C_1		A	1941.6	1944.2
		A	[b]	1894.1
$Mn(\eta^3\text{-}C_3H_5)(^{12}CO)(^{13}CO)_2$		A	1996.5	1997.5
C_1		A	[b]	1928.3
		A	[b]	1892.6
$Mn(\eta^3\text{-}C_3H_5)(^{12}CO)(^{13}CO)_2$		A'	2017.3	2019.0
C_s		A'	1916.9	1918.6
		A''	1882.6	1882.0
$Mn(\eta^3\text{-}C_3H_5)(^{13}CO)_3$		A'	1984.4	1985.3
C_s		A'	1908.8	1907.8
		A''	1882.6	1882.0

[a] Refined energy-factored CO stretching and interaction force constants ($N\ m^{-1}$) are: $K_1 = 1619.9$, $K_2 = 1540.2$, $k_{12} = 43.2$ and $k_{23} = 43.5$. [b] predicted band obscured by overlapping bands of other species.

Photolysis of $Mn(\eta^1\text{-}C_3H_5)(CO)_5$ in ^{13}CO dopes (5%) CH_4 matrices

Upon UV irradiation (filter B) of $Mn(\eta^1\text{-}C_3H_5)(CO)_5$ in a 5% ^{13}CO doped CH_4 matrices the complex was immediately converted to $Mn(\eta^3\text{-}C_3H_5)(CO)_4$ via loss of CO. Further UV irradiation resulted in the appearance of bands for the species proposed above to be $Mn(\eta^3\text{-}C_3H_5)(CO)_3$. Continued irradiation with UV and visible light caused the bands of ^{13}CO isotopically enriched species to emerge. UV and visible irradiation were then performed alternatively until satisfactory band positions and intensities of isotopically enriched products were obtained. None of the observed product bands could be matched to the calculated [22,23] band positions of the ^{13}CO labelled parent complex, i.e. $Mn(\eta^1\text{-}C_3H_5)(^{12}CO)_{5-n}(^{13}CO)_n$ ($n = 1\text{–}5$). A reasonable fit was, however obtained for the observed and calculated bands of a C_s symmetry $Mn(CO)_3$ fragment. This firmly established the identity of the proposed new photolysis species as $Mn(\eta^3\text{-}C_3H_5)(CO)_3$ (Table 2).

Photolysis of $Mn(\eta^1\text{-}C_3H_5)(CO)_5$ in N_2 and CO matrices

Infrared spectra from an experiment with $Mn(\eta^1\text{-}C_3H_5)(CO)_5$ isolated in an N_2 matrix are shown in Fig 3. At high dilution at ca. 12 K the spectrum of the parent

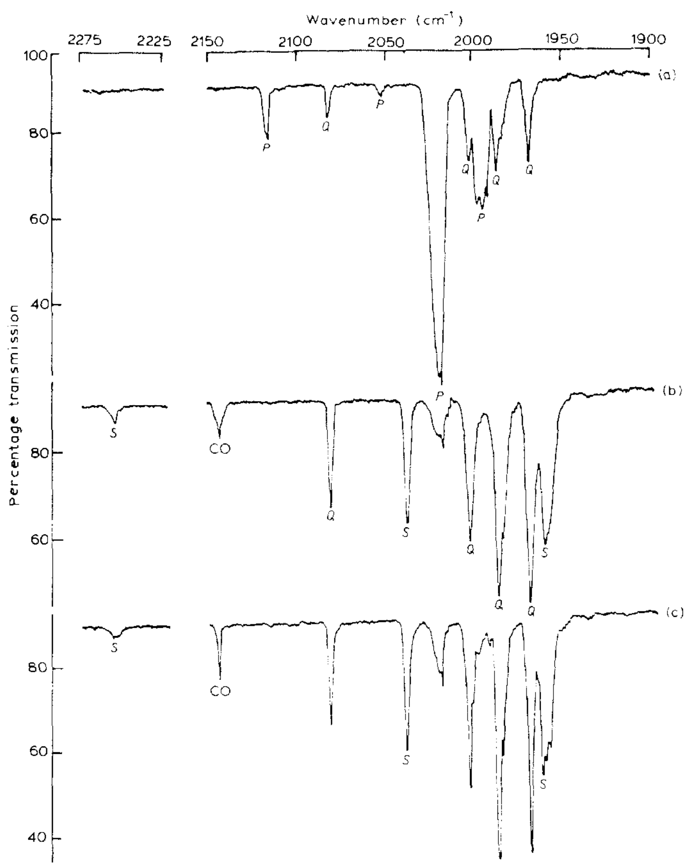


Fig. 3. Infrared spectra (Grubb Parsons Spectromajor) from an experiment with Mn(η^1-C_3H_5)(CO)$_5$ isolated at high dilution in an N_2 matrix at ca. 12 K: (a) after deposition, (b) after 30 min UV irradiation (filter D), and (c) after annealing to ca. 30 K. Labelled bands are: P = Mn(η^1-C_3H_5)(CO)$_5$, Q = Mn(η^3-C_3H_5)(CO)$_4$, S = Mn(η^3-C_3H_5)(CO)$_3$(N_2).

complex (Fig. 3(a)) is very similar to those in CH_4 and Ar matrices. Again, bands marked Q are observed in the starting spectrum and are due to Mn(η^3-C_3H_5)(CO)$_4$ present as an impurity.

A period of UV irradiation (filter d) produced a spectrum (Fig. 3(b)) showing increases in intensities of the Mn(η^3-C_3H_5)(CO)$_4$ bands and the appearance of four new bands at 2256.9, 2138.0 ('free' CO), 2018.8 and 1960.0 cm^{-1}. The band at 2256.9 cm^{-1} is in the region expected for NN stretching and can be confidently assigned to a terminal NN stretching model. With the production of 'free' CO and assigning the bands at 2018.8 and 1960.0 cm^{-1} as terminal CO stretching modes, the photoproduct can probably be identified as Mn(η^3-C_3H_5)(CO)$_3$(N_2). If Mn(η^3-C_3H_5)(CO)$_3$(N_2) adopts a C_s symmetry the third CO stretching band, which is expected, could accidentally coincide with the band at 1960.0 cm^{-1}, cf. Mo(η^5-C_5H_5)(CO)$_3$$CH_3$ [24] (ν(CO) at 2039.9 (A') and 1937.9 ($A' + A''$) cm^{-1}). Alternatively, if Mn(η^3-C_3H_5)(CO)$_3$(N_2) adopts a trigonal bipyramidal structure with the η^3-allyl and N_2 ligands in the axial positions, the three CO ligands would have C_{3v}

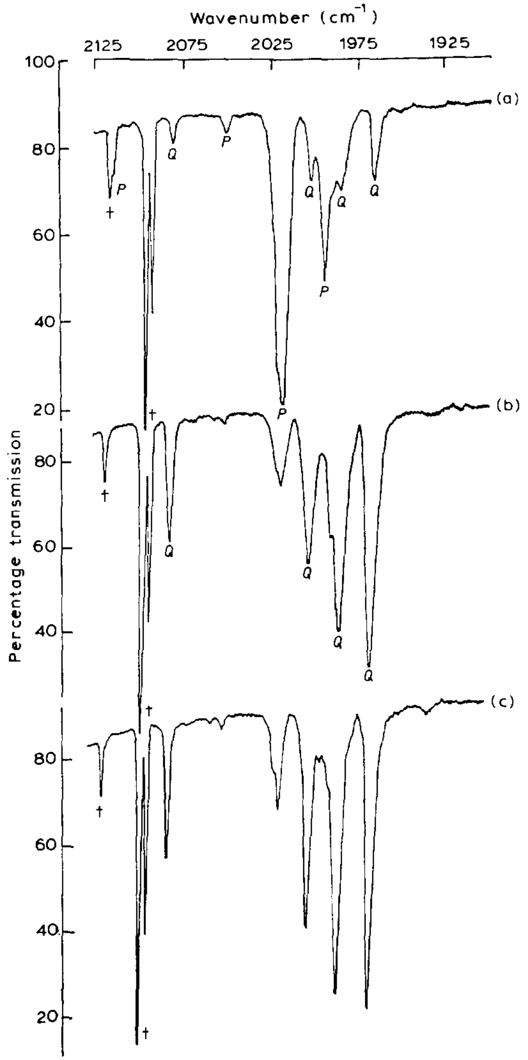


Fig. 4. Infrared spectra (Grubb Parsons Spectromajor) from an experiment with $Mn(\eta^1-C_3H_5)(CO)_5$ isolated at high dilution in a CO matrix at ca. 12 K: (a) after deposition, (b) after 30 min UV irradiation (filter D), and (c) after annealing to ca. 35 K. Bands marked with a dagger (†) are due to natural abundance ^{13}CO. Other bands are: $P = Mn(\eta^1-C_3H_5)(CO)_5$, $Q = Mn(\eta^3-C_3H_5)(CO)_4$.

local symmetry ($\nu(CO) = A_1 + E$) and in this case the 1960.0 cm^{-1} band could be the E mode band *.

In a CO matrix at ca. 12 K the infrared spectrum of $Mn(\eta^1-C_3H_5)(CO)_5$ after deposition is very similar to those in CH_4, Ar and N_2 matrices (Fig. 4(a)). After a

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* ^{13}CO exchange in the parent complex is not possible and attempts to photolyse $Mn(\eta^1-C_3H_5)(CO)_5$ in a ^{13}CO doped N_2 matrix have led to ^{13}CO enriched $Mn(\eta^3-C_3H_5)(CO)_4$ and no dinitrogen product. Thus, in the absence of ^{13}CO data, the exact structure of $Mn(\eta^3-C_3H_5)(CO)_3(N_2)$ could not be determined.

period of UV irradiation (filter D), the bands of Mn(η^3-C_3H_5)(CO)$_4$ increased at the expensive of the parent bands (Fig. 4(b)). No bands attributable to Mn(η^3-C_3H_5)(CO)$_3$ species were observed even after prolonged irradiation. On annealing the matrix, all the bands sharpened (Fig. 4(c)). Surprisingly, no evidence was observed for bands that could be attributed to a Mn(CO)$_5$ radical (ν(CO) at 2105.3 and 1987.6 cm^{-1} in a CO matrix [25]) nor was there any evidence for the reverse reaction (eq. 5).

$$\mathrm{Mn}(\eta^3\text{-}C_3H_5)(CO)_4 + CO \rightarrow \mathrm{Mn}(\eta^1\text{-}C_3H_5)(CO)_5 \qquad (5)$$

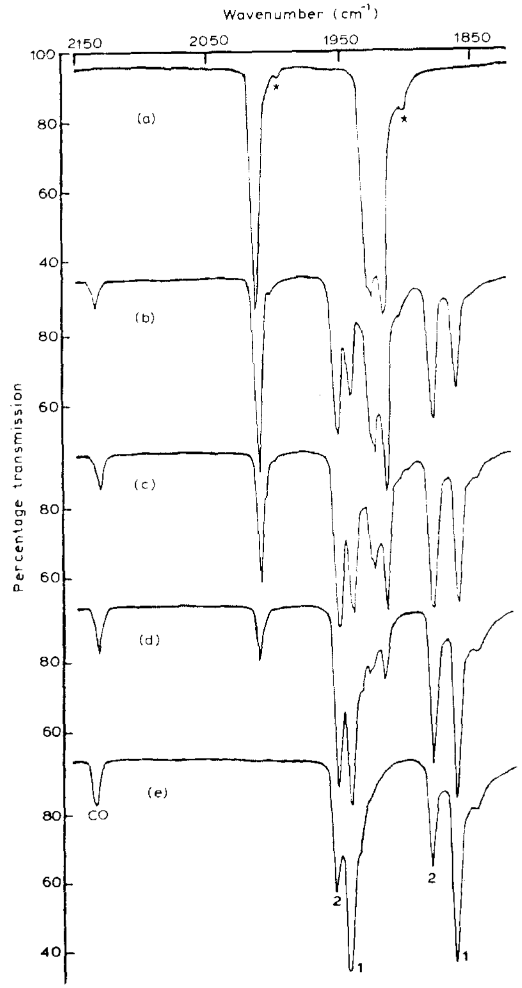


Fig. 5. infrared spectra (Grubb Parsons Spectromajor) from an experiment with W(η^1-C_3H_5)(η^5-C_5H_5)(CO)$_3$ isolated at high dilution in a CH_4 matrix at ca. 12 K: (a) after deposition, (b) after 10 min photolysis using low energy UV light (filter E), (c) after further 15 min photolysis with the same source, (d) after 20 min photolysis using UV light (filter A), and (e) after further 25 min photolysis with UV radiation. Bands marked with an asterisk (*) are due to W(η^1-C_3H_5)(η^5-C_5H_5)(^{12}CO)$_2$(^{13}CO) present in natural abundance. Bands marked **1** and **2** derive from photoproducts (see text).

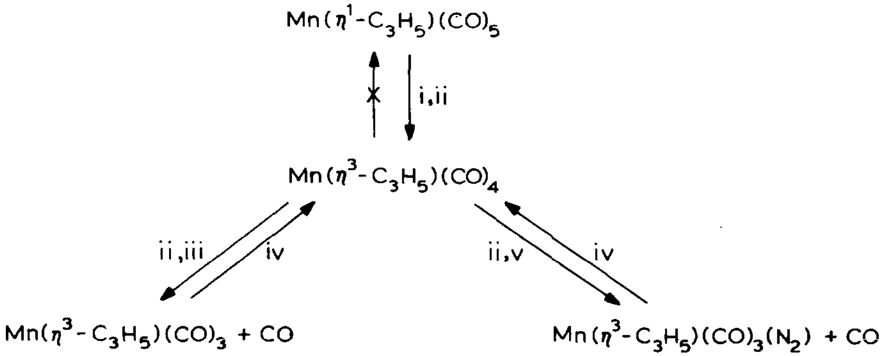
Photolysis of $W(\eta^1\text{-}C_3H_5)(\eta^5\text{-}C_5H_5)(CO)_3$ *in* CH_4 *matrices* *

The IR spectrum of $W(\eta^1\text{-}C_3H_5)(\eta^5\text{-}C_5H_5)(CO)_3$ isolated at high dilution in a CH_4 matrix (Fig. 5, Table 1) is very similar to that of $W(\eta^1\text{-}CH_2Ph)(\eta^5\text{-}C_5H_5)(CO)_3$ [26] in a CH_4 matrix. Irradiation with low energy UV light ($\lambda > 370$ nm, filter E) produced four new bands at 1960.2, 1951.8, 1882.5 and 1866.5 cm^{-1} (Fig. 5(b), Table 1) and a band for 'free' CO at 2138 cm^{-1}. A further period of irradiation (filter E) caused an increase in free CO, increases in all the new bands, and decreases in all the bands of the parent complex (Fig. 5(c)). The four new bands were demonstrated to belong to two different species because two bands (bands **1**, 1951.8 and 1866.5 cm^{-1}) decreased rapidly when the matrix was annealed. This annealing behaviour is exactly analogous to that of the 16-electron coordinatively unsaturated species $W(\eta^5\text{-}C_5H_5)(CO)_2R$ ($R = CH_3$, C_2H_5, C_3H_7, C_4H_9, Ph, $\eta^1\text{-}CH_2Ph$; $\nu(CO)$ ($R = \eta^1\text{-}CH_2Ph$) at 1941.4 and 1859.5 cm^{-1}; [24,26]). The bands **1** may, therefore, be assigned to the 16-electron species $W(\eta^1\text{-}C_3H_5)(\eta^5\text{-}C_5H_5)(CO)_2$. The other pair of bands (bands **2**, 1960.2 and 1882.5 cm^{-1}) may be assigned to the saturated π-allyl complex, $W(\eta^3\text{-}C_3H_5)(\eta^5\text{-}C_5H_5)(CO)_2$ by comparison with the solution IR data (1960 and 1880 cm^{-1}) [10,27]. Irradiation of the matrix with UV light (λ 320–390 nm, filter A) resulted in a decrease in the bands of $W(\eta^3\text{-}C_3H_5)(\eta^5\text{-}C_5H_5)(CO)_2$ and a growth in the bands of $W(\eta^1\text{-}C_3H_5)(\eta^5\text{-}C_5H_5)(CO)_2$ (Figs. 5(d) and 5(e)).

Discussion

The photochemical reactions of the allyl complexes $Mn(\eta^1\text{-}C_3H_5)(CO)_5$ and $W(\eta^1\text{-}C_3H_5)(\eta^5\text{-}C_5H_5)(CO)_3$ isolated at high dilution in various gas matrices at ca. 12 K are summarised in Schemes 1 and 2, respectively.

The low temperature matrix isolation experiments seem to indicate that the loss of CO and $\eta^1\text{-allyl} \rightarrow \eta^3\text{-allyl}$ rearrangement occur simultaneously for $Mn(\eta^1\text{-}C_3H_5)(CO)_5$. The creation of a vacant coordination site close to the allyl ligand, e.g. loss of a *cis* equatorial CO ligand, opens the way for donation of an extra electron pair from free double-bond of the η^1-allyl ligand to satisfy the 18-electron rule



SCHEME 1. (i) CH_4, Ar, N_2 or CO; (ii) UV irradiation; (iii) CH_4 or Ar; (iv) Visible irradiation or annealing; (v) N_2.

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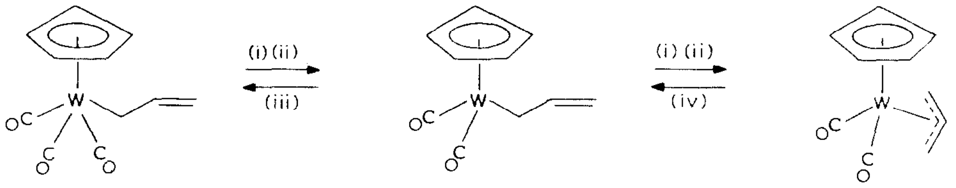
* In common with $W(\eta^1\text{-}CH_2Ph)(\eta^5\text{-}C_5H_5)(CO)_3$ [16,26] only decarbonylation and $\sigma \rightarrow \pi$ rearrangement was observed for N_2 and CO matrices and so there is nothing new to report for these matrices.



SCHEME 2. (i) CH_4, Ar, N_2 or CO; (ii) Far UV irradiation; (iii) Annealing; (iv) Mid-UV irradiation.

requirement of the Mn. Surprisingly, no evidence for a 16-electron intermediate, $Mn(\eta^1\text{-}C_3H_5)(CO)_4$, has been observed, cf. the observation of $Mn(CO)_4COCH_3$ and $Mn(CO)_4CH_3$ on photolysis of $Mn(CO)_5(COCH_3)$ and $Mn(CO)_5CH_3$ [15,19], respectively. However, other π-hydrocarbon manganese complexes seem to prefer re-arrangements which afford 18-electron species, e.g. successive photo-ejection of CO from $Mn(\eta^1\text{-}C_7H_7)(CO)_5$ in Ar and CH_4 matrices yielded $Mn(\eta^3\text{-}C_7H_7)(CO)_4$ and $Mn(\eta^5\text{-}C_7H_7)(CO)_3$ with no sign of the 16-electron species $Mn(\eta^1\text{-}C_7H_7)(CO)_4$ and $Mn(\eta^3\text{-}C_7H_7)(CO)_3$ [28] while photolysis of $Mn(\eta^5\text{-}C_5H_7)(CO)_3$ in a CO matrix gave the ring-slip 18-electron product species $Mn(\eta^3\text{-}C_5H_7)(CO)_4$ [29].

The observation of $\eta^1 \rightarrow \eta^3$ conversion in all matrices (CH_4, Ar, N_2, CO) suggests that this is a very facile process. The irreversibility of the $\eta^1 \rightarrow \eta^3$ rearrangement for Mn is in contrast to eq. 4 for Co and also for the W allyl complexes (see below). However, the irreversibility is consistent with the gas-phase UV photoelectron spectroscopic [30] and X-ray photoelectron spectroscopic [31] studies which concluded that the η^3-allyl Mn complex is more stable than the η^1-allyl complex. Further evidence for the irreversibility of the $\eta^1 \rightarrow \eta^3$ rearrangement is that no ^{13}CO was incorporated into $Mn(\eta^1\text{-}C_3H_5)(CO)_5$ when it was photolysed in ^{13}CO doped CH_4 matrices whereas the η^3-allyl complex did show ^{13}CO incorporation. Consistent with this exchange is the observation that a CO ligand can be photo-ejected from $Mn(\eta^3\text{-}C_3H_5)(CO)_4$ to give the coordinatively unsaturated species $Mn(\eta^3\text{-}C_3H_5)(CO)_3$. The reactivity of this species is demonstrated by its recombination with CO to produce $Mn(\eta^3\text{-}C_3H_5)(CO)_4$, the suppression of its formation in CO matrices, and reaction with N_2 to form $Mn(\eta^3\text{-}C_3H_5)(CO)_3(N_2)$. The high value of ν(NN) (2256.9 cm^{-1}) for $Mn(\eta^3\text{-}C_3H_5)(CO)_3(N_2)$ and its reversibility indicate that it is unlikely to be stable at ambient temperatures, cf. $Mn(\eta^5\text{-}C_5H_5)(CO)_2(N_2)$ has ν(NN) at 2169 cm^{-1} in solution [32] and 2175 cm^{-1} in a N_2 matrix [33].

In contrast to the η^1-allyl manganese complex but in accord with the cobalt complex (eq. 4), the η^1-allyl tungsten complex gave both the 16-electron species $W(\eta^1\text{-}C_3H_5)(\eta^5\text{-}C_5H_5)(CO)_2$ as well as the fully rearranged 18-electron species, $W(\eta^3\text{-}C_3H_5)(\eta^5\text{-}C_5H_5)(CO)_2$. It is noteworthy that the $\eta^1 \rightarrow \eta^3$ rearrangement is reversible, i.e. the species $W(\eta^1\text{-}C_3H_5)(\eta^5\text{-}C_5H_5)(CO)_2$ has considerable intrinsic stability. The reversibility however, seems to preclude other ligands entering since no incorporation of N_2 or C_2H_4 took place when these ligands were doped into matrices; this behaviour is analogous to that of the η^1- and η^3-benzyl complexes $W(\eta^1\text{-}CH_2Ph)(\eta^5\text{-}C_5H_5)(CO)_3$ and $W(\eta^3\text{-}CH_2Ph)(\eta^5\text{-}C_5H_5)(CO)_2$ [26]. An important fact to emerge from the allyl tungsten complex is that the $\eta^1 \rightarrow \eta^3$ rearrangement is a two step process but whether both steps require a photon, where the reaction is photochemical, has yet to be determined. The discovery of a two step process may have implications for kinetic studies.

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